

Article

Investigation on the La Replacement and Little Additive Modification of High-Performance Permanent Magnetic Strontium-Ferrite

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Abstract: In this work, an experiment was carried out to investigate the preparation condition of anisotropic, Fe-deficient, *M*-type Sr ferrite with optimum magnetic and physical properties by changing experimental parameters, such as the La substitution amount and little additive modification during fine milling process. The compositions of the calcined ferrites were chosen according to the stoichiometry $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$, where *M*-type single-phase calcined powder was synthesized with a composition of $x = 0.30$. The effect of CaCO_3 , SiO_2 , and Co_3O_4 inter-additives on the Sr ferrite was also discussed in order to obtain low-temperature sintered magnets. The magnetic properties of $B_r = 4608$ Gauss, $H_c = 3650$ Oe, $H_c = 3765$ Oe, and $(BH)_{\max} = 5.23$ MGOe were obtained for Sr ferrite hard magnets with low cobalt content at 1.7 wt%, which will eventually be used as high-end permanent magnets for the high-efficiency motor application in automobiles with $B_r > 4600 \pm 50$ G and $H_c > 3600 \pm 50$ Oe.

Keywords: magnet; strontium-ferrite; replacement; cobalt; additives; fine mill; motor; automobile



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1. Introduction

Hexagonal magneto-plumbite-type strontium ferrite ($\text{SrFe}_{12}\text{O}_{19}$) has material characteristics, such as a stable crystal structure, high coercivity and magnetic energy product, and magnetic anisotropy (K_1) [1], so it is widely used in permanent magnet motors and various electronic devices, which is an important basic functional material in the electronics industry. In recent years, with the development of the green economy and environmental protection industry, the miniaturization and high-performance requirements of electronic components have gradually increased, accompanied by strong demand for the miniaturization and high performance of magnets. High-performance permanent magnet ferrites with high remanence (B_r), high coercivity (H_c), and high magnetic energy product ($(BH)_{\max}$) are new market needs for the rapid development of the world's electronic information and automobile industries [2,3]. In order to improve the various physical and magnetic properties of strontium ferrite, research is mainly carried out on two aspects: formula and process conditions. After years of exploration and research, it has been discovered that simply by optimizing the process parameters of ferrite, such as the particle size and distribution after ball milling, the calcination temperature curve, the sintering temperature curve, and the compression molding process, some performance indexes of strontium ferrite can be optimized to a certain level. However, compared with its various theoretical values, there is still a big gap [4–9]. In a material, by doping a small amount of other elements or compounds, the material will produce specific optical, electrical and magnetic

properties. For strontium ferrite, the proper amount of doping can also improve its magnetic and physical properties, but it is of great significance for the determination of the doping amount and doping method. How the magnetic properties of permanent ferrites through ion substitution can be improved has become an important way to accelerate the performance of permanent ferrites. This starts from the crystal structure and microscopic morphology, uses the basic theory of micro-magnetoelectronic spin to optimize ion substitution, and fundamentally promotes the research and developmental process of high-performance permanent magnet ferrites [10–15]. In recent studies, a significant improvement has been made in $\text{SrFe}_{12}\text{O}_{19}$ ferrite by a combined replacement of La^{3+} in Sr^{2+} site and Co^{2+} in Fe^{3+} , and the simultaneous substitution of lanthanum and cobalt could obviously enhance the intrinsic coercivity iH_c when keeping the remanence B_r invariant. However, past research has often designed a calcined La-Co base formula composition to acquire large B_r and large iH_c at the same time [13–19]. It ought to be noticed that the design of the formula requires the participation of valuable metal component cobalt to be used in the calcination formula in the form of oxide, such as Co_3O_4 , which has a big hazard of mass production and greater cost. Previously, several literatures have been conducted with the goal of making Sr ferrite either with lower cobalt content or without cobalt [5,20]; however, such permanent materials possess lower magnetic characteristics. Furthermore, finer magnetic powder mill ($<0.65\ \mu\text{m}$) and wet magnetic molding processes give magnets better performance due to a single magnetic domain grain size and higher alignment. Yet, for wet magnetic molding, it would be hard to press slurry in the mold; thus, the conventional processing technique nearly reached its limit [21–23]. As far as the current situation is concerned, the use of cobalt in combination with an extensive range of critical businesses and technical applications is of essential vital importance, and therefore its value has been continuously increased. Regarding the issue above, it is critical to develop a Fe-deficient M-type Sr ferrite calcination formula without any addition of cobalt during the calcination process and as little cobalt used in the secondary additive as possible to modify the magnetic properties of M-type ferrite hard magnets. In this study, a non-stoichiometric formula composed of $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ was chosen to form Fe-deficient M-type Sr ferrites with $x = 0.30$. For this formula, $n = 11.4$, where n is the mole ratio of (La+Sr): (Fe). Among the calcined formula, no cobalt element is used in the calcined powder, which can reduce the cost of M-type ferrite permanently. When the mole ratio n is smaller than 12, the ferrites take an Fe-deficient formula. Differently from past studies, the results in this work have the following merits. First, the valuable metal component, cobalt, was not used in the main calcined formula; thus, the price of calcining powder was cheap, which was beneficial to mass production. Next, the secondary additive, such as Co_3O_4 , CaCO_3 , and SiO_2 doped after calcining are profoundly adjustable. While Co_3O_4 was added with CaCO_3 and SiO_2 , the amount of Co_3O_4 doped as the secondary additive after calcining is little, allowing it to be more economical to modify the magnetic properties of Sr ferrite and enhance mass production. In this work, a calcined formula without precious cobalt is brought to execution. The magnetic properties could be modified by a little amount of Co_3O_4 with two other important additives, CaCO_3 and SiO_2 , added after calcining instead of during the calcination step to satisfy customers' need for permanent ferrite magnet with high performance, low material prices, small batch production, easy manufacturing, large process-adjusting windows, and excellent economy. Our experimental results found that with a Fe-deficient calcined formula with a “Cobalt-free” recipe design and optimized process parameters, magnetic performance was obtained as follows:

$$B_r = 4608 \text{ Gauss, } iH_c = 3710 \text{ Oe,}$$

$$iH_c = 3765 \text{ Oe, and } (BH)_{\text{max}} = 5.23 \text{ MGOe}$$

2. Experimental Procedure

2.1. Sample Preparation

In this study, Fe-deficient M-type Sr ferrite magnets have been synthesized by the conventional ceramic method. Nonstoichiometric compositions were selected on the basis of the chemical composition $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$, where La content (x) varied from 0.28 to 0.32, and Sr content ($1-x$) from 0.70 to 0.74. The raw material Fe_2O_3 is manufactured by the acid recycle Ruthner process of the China Steel Corporation (CSC) in Taiwan [7,24] with high purity (>99.5%) and Specific Surface Area (SSA) = $3.5 \pm 0.2 \text{ m}^2/\text{g}$. The SrCO_3 with >98% purity and different particle sizes of 1.0~2.5 μm was used as another starting material to clarify the influence of its particle size on the magnetic properties of Sr ferrite. First, the raw material Fe_2O_3 , SrCO_3 , and La_2O_3 powders and the additive CaCO_3 were wet-mixed by an attritor, and then granulated for calcination. A single phase of submicron-sized Sr ferrite powder was prepared by calcining in an electric furnace at $1270 \pm 5^\circ\text{C}$ for 1 h in air at increments of 10°C . The calcination granules were vacillated vigorously in a vibration mill to achieve a powder size of approximately $2.2 \pm 0.1 \mu\text{m}$ on average. Next, the additives CaCO_3 , SiO_2 , and Co_3O_4 were doped in different concentrations by fine-milling the mixture for about 9 h in a stainless steel ball-miller before sintering. This step guarantees a narrower particle-size distribution with a mean size about $0.70 \pm 0.05 \mu\text{m}$ measured by a Fisher subsieve sizer (Fisher, Waltham, MA, USA), which is important for achieving good performance. Here, we further explain why the two-stage grinding process was performed in the experiment. For the traditional manufacturing process of permanent ferrite materials, the two-stage milling process will be carried out in sequence. These two different milling processes have different purposes for the preparation of permanent ferrite. For the first stage of milling, we can call it pulverization, or “coarse milling”. This coarse milling is usually carried out by a vibrating mill, which is a more vigorous process and able to grind the calcined granules from a centimeter-level size to μm -level size in a shorter time. We usually grind the calcined granules to a powder size of about $2.2 \pm 0.1 \mu\text{m}$ on average through this “coarse milling” process. Because the first stage of the milling process already ground the calcined granules to a relatively smaller size, the second stage of the milling process, that is, the fine milling process, is usually used to grind the magnetic powder to a smaller size of less than $1 \mu\text{m}$ ($0.70 \pm 0.5 \mu\text{m}$ in this study) by a ball mill to fit the permanent magnet process requirements. Because the ball milling process is a relatively mild grinding process, it can achieve a narrow and single-peak magnetic particle size distribution, which is necessary for achieving better magnetic performance, but will take a longer time. However, if we do not grind the calcined granules through the coarse milling process first, but directly use the ball mill to grind, this will cause the required grinding time to become quite long, and it will not be easy to achieve the aforementioned particle size distribution results. The milled slurry was pressed into tablets of $\Phi 26.5 \text{ mm}$ in diameter and 13 mm in height under a magnetic field of about 1.5 Tesla and 100 MPa pressure (according to the Japanese Industrial Standard, JIS C2501). The pressed tablets were sintered at a peak temperature of $1230 \pm 5^\circ\text{C}$ for 1 h.

2.2. Measurements

X-ray diffraction (XRD, Cu-K α radiation) was used for the phase identification of the calcined magnetic powder. The powder size distribution of SrCO_3 was measured by the Sympatec laser-scattering system under the sample analysis volume of 0.5 g using a dry dispersion unit (system Rodos). The magnetic properties (B_r , iH_c , and $(BH)_{\text{max}}$) of the sintering magnets were measured at room temperature by the NIM-2000 HF Hysteresis graph meter (China National Measuring Science Research Institute) on the polished discs. The bH_c describes the magnetic field which makes the B distribution in the magnet change direction. The bH_c is smaller than iH_c , which is the field necessary to demagnetize the polarization or magnetization to zero. Usually, we use iH_c to represent the intrinsic magnetic properties of permanent magnet materials. Scanning electron microscopy (SEM;

Zeiss) was used to analyze the ceramic microstructures on the polished and thermally etched faces of the magnets (perpendicular to the applied pressure and field).

3. Result and Discussion

Effect of Calcined Ferrite Stoichiometry

The general formula of *M*-type ferrite is $A\text{Fe}_{12}\text{O}_{19}$, where $A = \text{Ba}$ or Sr , and a part of these elements can be replaced by rare-earth elements. Among them, a part of Fe could be substituted by cobalt (Co) to obtain better magnetic performance that would result in high intrinsic magnetization M_s and anisotropic magnetic field strength H_A [13–19]. Besides, the element at the A position can be substituted by other rare-earth elements, such as La , since La^{3+} (1.17 Å), Ba^{2+} (1.22 Å), and Sr^{2+} (1.32 Å) share almost the same radius. La has the highest solid solution limit for *M*-type ferrites, and the substitution of La at the A position can enhance the solid content of Co that substitutes Fe , which is critical and beneficial to the improvement of the magnetic characteristics of Sr ferrite [11,13,16,25]. To investigate the influence of the amount of La substituted for Sr in the calcined ferrite on the magnetic properties, a non-stoichiometric formula composed of $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ was selected to form Fe -deficient Sr base *M*-type ferrite with $x = 0.28\sim 0.32$. It can be seen from the experimental results in Figure 1 that the substitution amount of La_2O_3 in the calcined ferrite must be sufficient to react with cobalt added during the fine-milled process to promote the diffusion of Co ions in the sintering reaction to achieve better magnetic properties. When $x = 0.32$, the level of $B_r = 4536\text{G}$ and $iH_c = 4362\text{Oe}$ can be obtained. It can be clearly determined that the higher the amount of La_2O_3 in the calcined ferrite, the higher the B_r and iH_c . However, if the amount of La_2O_3 in the calcined ferrite is too high, it will cause a mismatch with the Co added after calcination, resulting in a decrease in magnetic properties [24]. The X-ray diffraction patterns of the Sr ferrite *M*-type ferrite $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ calcined powders with $x = 0.28\sim 0.34$ are given in Figure 2. It can be seen that the XRD patterns of the magnetic powders with La content (x) = 0.28~0.34 and Sr content ($1-x$) = 0.66~0.72 are all in good agreement with the Sr base *M*-type ferrite JCPDS card no. 84-1531 and illustrate a single-phase hexagonal structure.

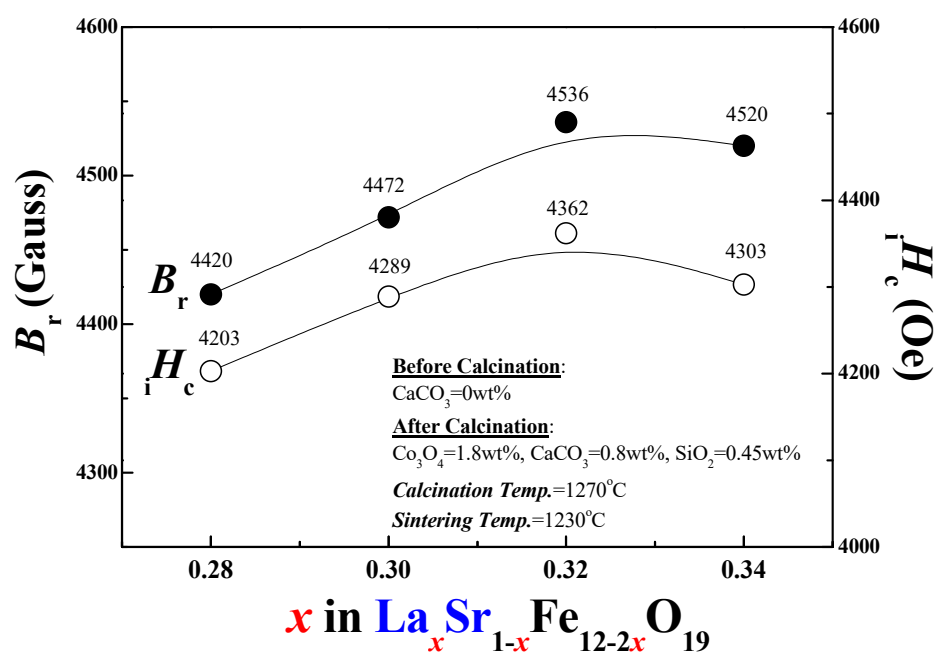


Figure 1. Dependence of B_r and iH_c of the fabricated sintered magnet on the x value of the formula $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ calcined ferrite.

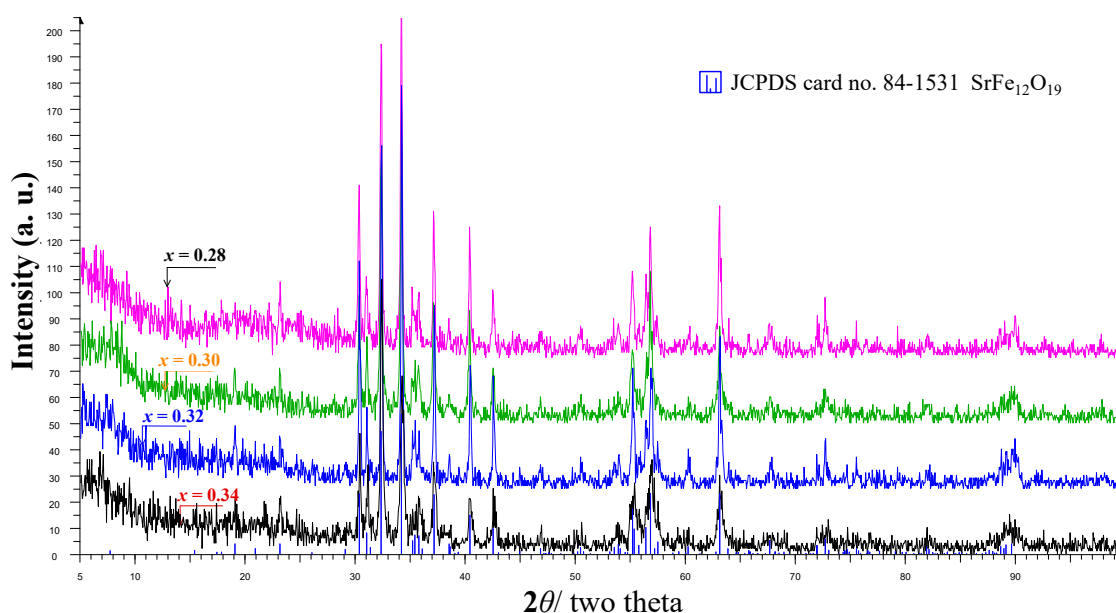


Figure 2. XRD patterns of the ferrite $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ calcine powders with La content (x) from 0.28 to 0.34, and Sr content ($1-x$) from 0.66~0.72.

In order to investigate the influence of the main raw material SrCO_3 with different particle sizes on the magnetic properties, two different particle sizes of SrCO_3 are used for experiments in this work. Table 1 shows the particle size analysis results, and Figure 3 shows the particle size distribution, where both were measured by the Sympatec laser scattering system under the sample analysis volume of 0.5 g. The SEM micrograph of SrCO_3 powders is shown in Figure 4. From the above results, it can be found that the morphology and sizes of the two different types of SrCO_3 are very different. Figure 5 shows an SEM of the $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ calcine powders with two different types of SrCO_3 as the raw material. From the results of Figure 6, it can be observed that if the SrCO_3 with finer particle size (expressed by the D_{50} value in Table 1) is used as the main raw material, the B_r of Sr ferrite will decrease significantly, while the iH_c will increase slightly. Corresponding to the SEM results of the calcined magnetic powder in Figure 5, it could be found that the calcined magnetic powder with a finer particle size of SrCO_3 as the main raw material has smaller grains of approximately 1~1.5 μm , which also causes the remanence B_r to be relatively low. In contrast, the calcined magnetic powder with a coarser particle size with SrCO_3 as the main raw material has a larger size of approximately 1.5~3 μm and tends to have a relative hexagonal plate, and its corresponding magnetic properties are also better.

Table 1. The particle size analysis results of the two different types of raw material SrCO_3 .

	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
SrSO_3 (Coarse Particle)	0.70 ± 0.02	2.50 ± 0.02	6.10 ± 0.02
SrSO_3 (Coarse Particle)	0.50 ± 0.02	1.00 ± 0.02	2.30 ± 0.02

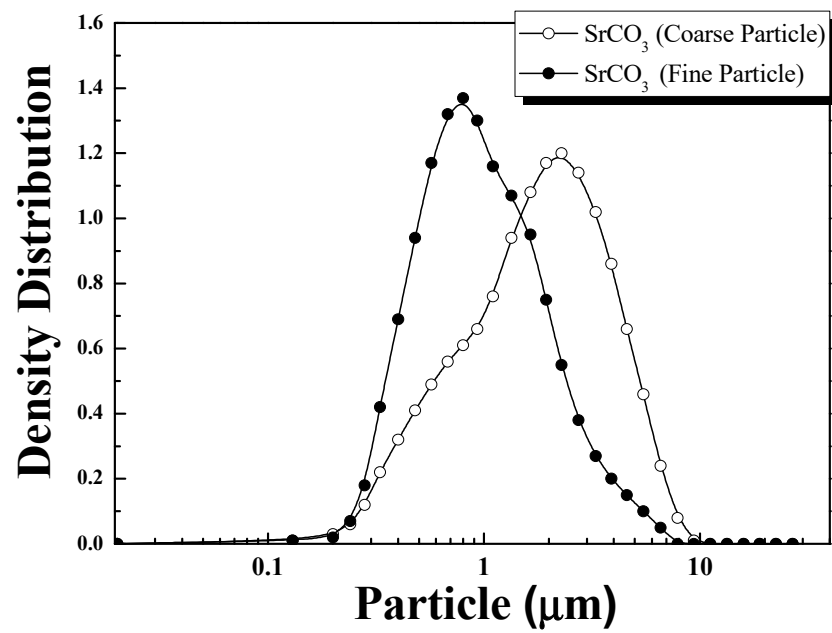


Figure 3. Particle size distribution of two different raw material SrCO_3 measured by the Sympatec laser scattering system.

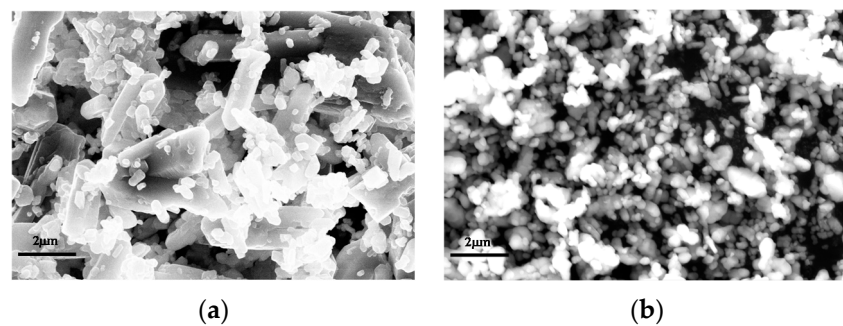


Figure 4. The SEM micrograph of two different raw material SrCO_3 powders: (a) coarse-particle SrCO_3 , (b) fine-particle SrCO_3 .

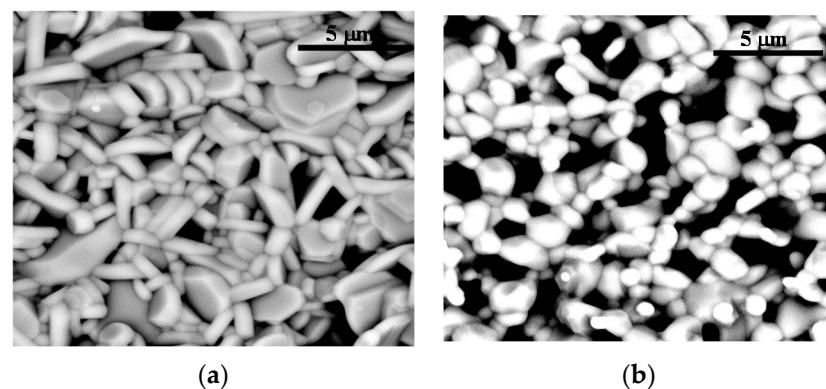


Figure 5. The SEM of the $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ calcined powders with two different particle sizes of SrCO_3 as the raw material: (a) coarse-particle SrCO_3 , (b) fine-particle SrCO_3 .

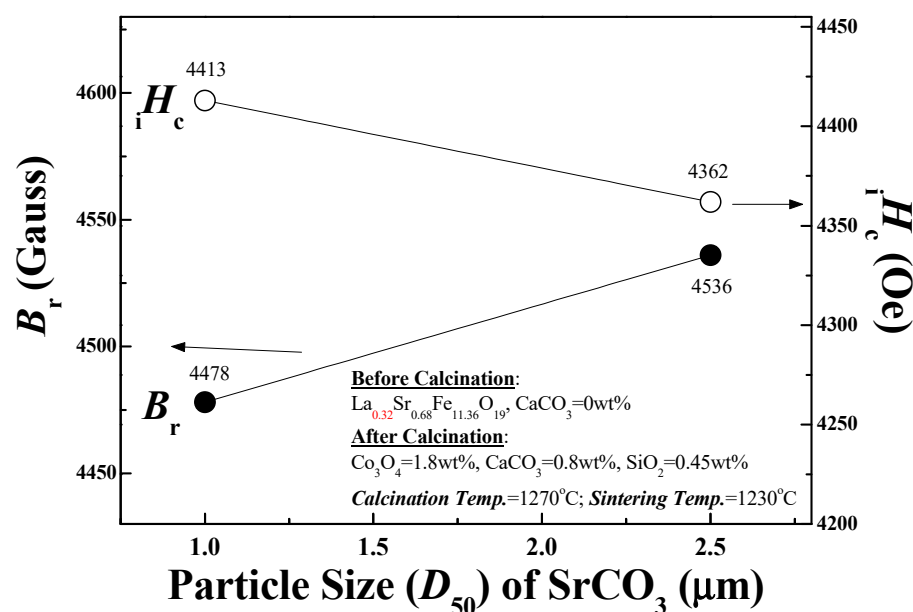


Figure 6. Magnetic properties of Sr ferrite with different particle sizes of raw material SrCO_3 .

The additive CaCO_3 could promote densification and uniform grain growth of hard ferrite, resulting in high remanence, but at the same time, iH_c must be sacrificed [24–26]. Enhancement of B_r could also be obtained by using Co_3O_4 in calcined material, and Co_3O_4 reduces iH_c much better than CaCO_3 , but the cost of Co_3O_4 is much higher than adding CaCO_3 . Therefore, this study discusses the effect of adding CaCO_3 before calcination on the improvement of magnetic properties. It can be seen from the comparison of the magnetic properties in Figure 7 that the addition of CaCO_3 before calcination can further increase B_r , but excessive CaCO_3 will cause a decrease in both B_r and iH_c , especially in iH_c . The main reason for the decrease of B_r due to excessive CaCO_3 is caused by too much non-magnetic phases in the calcined ferrite. Here, it is more appropriate to control the addition of CaCO_3 at 0.15% before calcination.

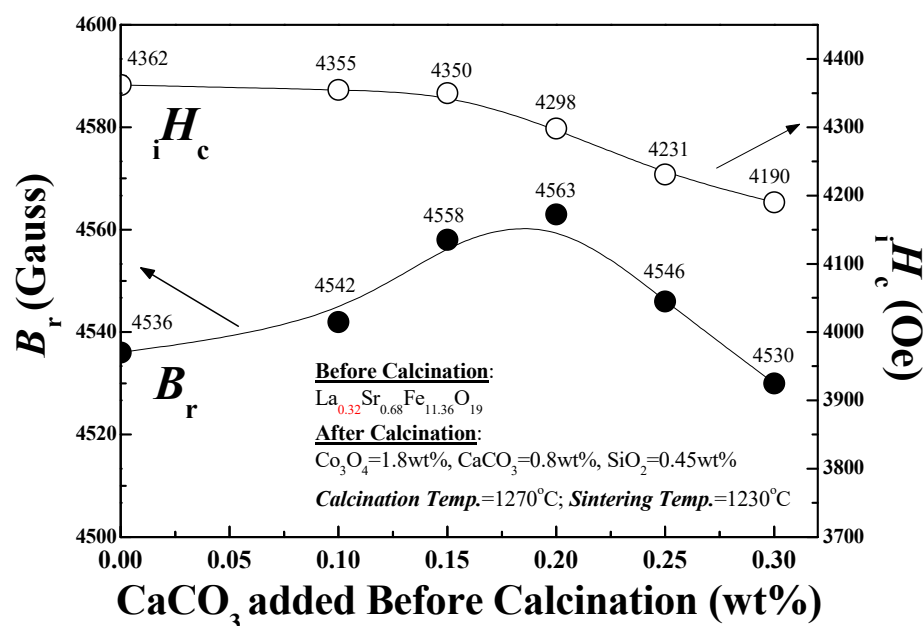


Figure 7. Dependence of B_r and iH_c of the sintered magnet on the amount of CaCO_3 added in the $\text{La}_{0.32}\text{Sr}_{0.68}\text{Fe}_{11.36}\text{O}_{19}$ calcined ferrite.

For permanent ferrite, the cost of La_2O_3 used for production of the magnet accounts for more than 10% of the total raw material cost. This study wishes to reduce the amount of La_2O_3 in the calcined ferrite to further reduce the total cost, but the magnetic properties must also be considered. The effect of CaCO_3 added before calcination on the magnetic properties is discussed above. In this section, in order to modify the magnetic properties after reduced La in the calcined formula, the influence of CaCO_3 added after calcination is investigated. The abnormal grain growth with a severe duplex structure is usually observed in M -type ferrites without additives, and is more obvious at a sintering temperature higher than 1200°C . SiO_2 can be used as a little additive to form a liquid phase for suppressing grain growth and enhancing the coercivity of hard ferrite [27,28]; however, a decreased sintered density results in decreased B_r . Thus, the simultaneous addition of CaCO_3 and SiO_2 after calcination is needed for moderating grain growth inhibition and promoting the sintered density [20,27,28]. It can be seen from the experimental results in Figure 8 that while x (La content) decreases from 0.32 to 0.30, the overall magnetic properties are significantly improved by the combined addition of CaCO_3 and SiO_2 after calcination. When $\text{CaCO}_3 = 0.7 \text{ wt}\%$ and $\text{SiO}_2 = 0.25 \text{ wt}\%$ added after calcination, the overall magnetic properties can reach a better state, which met the requirements of high-efficiency motor applications in automobiles with $B_r > 4600 \pm 50 \text{ G}$ and $iH_c > 3600 \pm 50 \text{ Oe}$ [29].

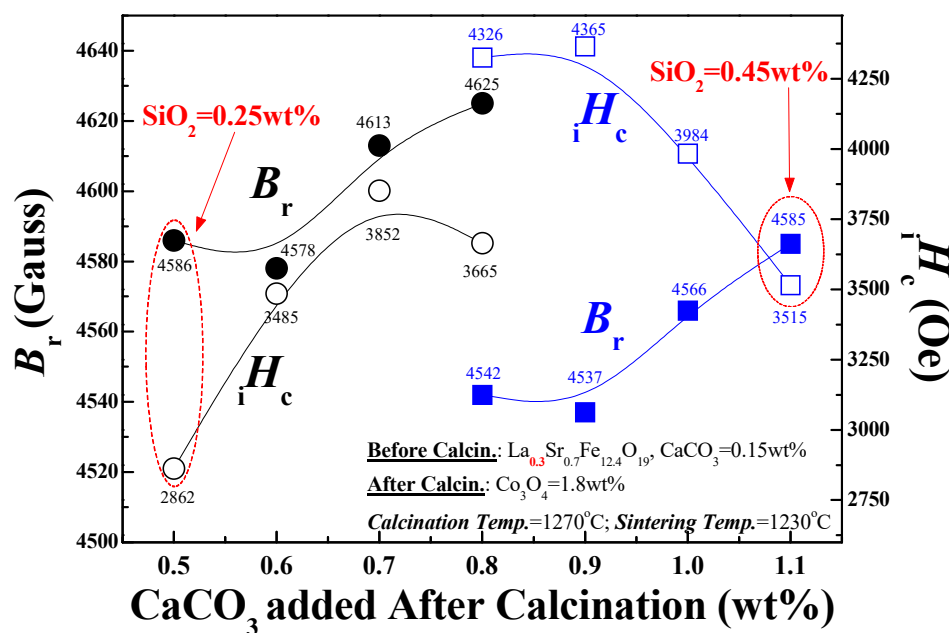


Figure 8. Dependence of B_r and iH_c of the sintered magnet on the amount of CaCO_3 added after the calcination process.

In order to improve the magnetic performance of the sintered ferrite magnet, both La and Co must be used at the same time to increase the reactivity of Co^{2+} with La^{3+} . If only La is contained in the permanent magnet ferrite, the effect of improving B_r and iH_c will not be obvious. This is because when La and Co undergo a substitution reaction in the permanent ferrite, the ratio of La to Co needs to reach a certain value, which is not suitable for values which are too large or too small [3,11–18]. Past studies usually designed a calcining La-Co system material formula to simultaneously achieve high B_r and high iH_c [3,11–18]. It should be noticed that this design of the formula requires the participation of the precious metal element of cobalt to be doped in the calcining formula, which may result in lower production flexibility, big mass-production hazards, and greater costs. In this study, cobalt was added as a little additive after the calcination process, and replaced Fe during the sintering process. From the result shown in Figure 9, the magnetic properties of Sr ferrite are moderately modified by Co_3O_4 simultaneously added with CaCO_3 and SiO_2 .

after calcination. At a lower amount of Co_3O_4 added after calcination ($\text{Co}_3\text{O}_4 = 1.7 \text{ wt}\%$), the goal of $B_r > 4600 \pm 50 \text{ G}$ and $iH_c > 3600 \pm 50 \text{ Oe}$ could be achieved at the same time.

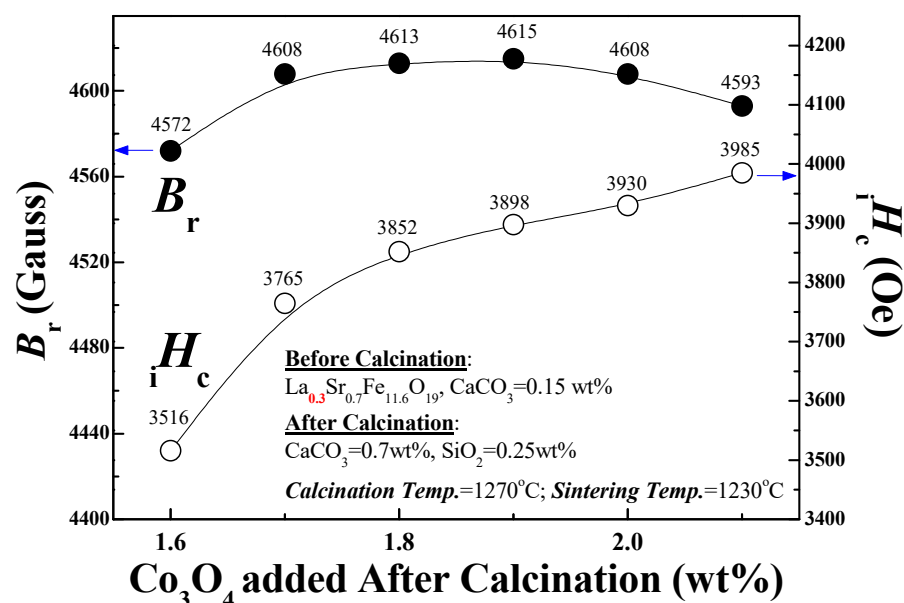


Figure 9. Dependence of B_r and iH_c of the sintered magnet on the amount of Co_3O_4 added after the calcination process.

Figure 10 presents the micromorphology of the ferrite $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{11.4}\text{O}_{19}$ sintered magnet at 1230°C with additive $\text{CaCO}_3 = 0.7 \text{ wt}\%$, $\text{SiO}_2 = 0.25 \text{ wt}\%$ and $\text{Co}_3\text{O}_4 = 1.7 \text{ wt}\%$ added after calcination. The grains in the magnet are plate-shaped, and the normal direction of plate-like grains harmonizes with the easy magnetization axis (i.e., C-axis). The alignment of the pressed powder was not annihilated during the sintering process and has good uniformity of grain size approximately smaller than $2 \mu\text{m}$; thus, the grains would be oriented and grown, bringing about the high performance of the sintering ferrite magnets, which can also be observed from the B-H hysteresis curves shown in Figure 11. The magnetic results obtained in this study are better than traditional Sr-La-Co ferrites [3,16–18], and help to achieve the purpose of high-end permanent magnets and large-scale industrial production.

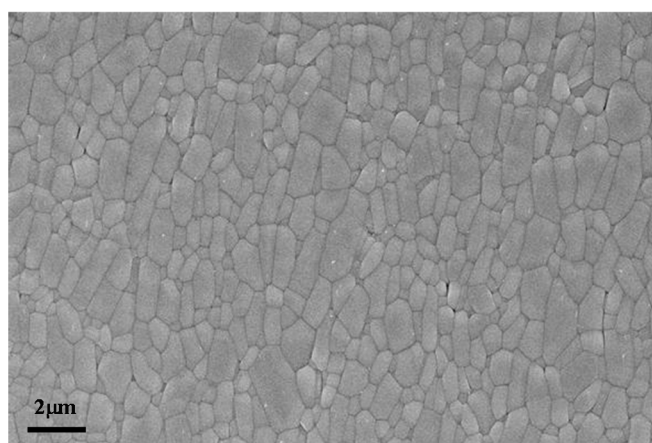


Figure 10. The SEM of the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{11.4}\text{O}_{19}$ sintered magnet with additive $\text{CaCO}_3 = 0.7 \text{ wt}\%$, $\text{SiO}_2 = 0.25 \text{ wt}\%$ and $\text{Co}_3\text{O}_4 = 1.7 \text{ wt}\%$ added after calcination.

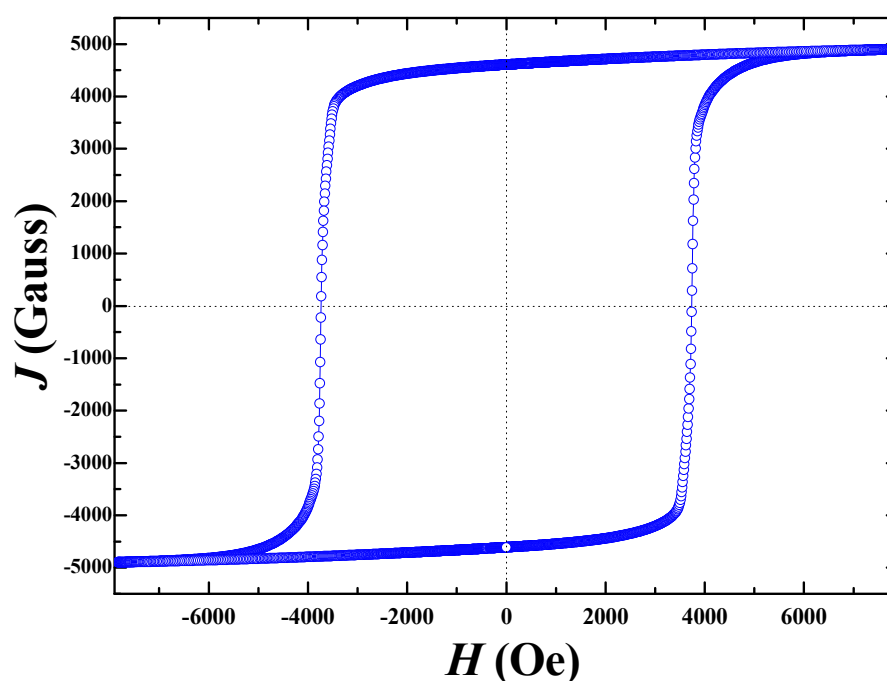


Figure 11. The B-H hysteresis curve of the $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{11.4}\text{O}_{19}$ sintered magnet with additive $\text{CaCO}_3 = 0.7 \text{ wt\%}$, $\text{SiO}_2 = 0.25 \text{ wt\%}$ and $\text{Co}_3\text{O}_4 = 1.7 \text{ wt\%}$ added after calcination.

4. Conclusions

In this study, the ferrite formula and process technique of high-performance anisotropic Fe-deficient Sr base *M*-type ferrite magnets were successfully developed, and the magnetic characteristics, such as B_r and iH_c , were obviously ameliorated. We especially emphasize that the calcining material formula of $\text{La}_x\text{Sr}_{1-x}\text{Fe}_{12-2x}\text{O}_{19}$ developed by this research does not include the precious metal cobalt, the amount of La_2O_3 in the calcined ferrite is small, and a little amount of the additive Co_3O_4 is added after the calcination process, which overcomes high-cost technical bottlenecks, such as excessive La_2O_3 and Co_3O_4 contained in the magnet in order to achieve high characteristics in the past, and we comprehensively improve magnetic characteristics and production efficiency. Besides, the incorporation of CaCO_3 , SiO_2 , and Co_3O_4 in the fine-milling step is well-suited for promoting the intrinsic magnetic properties, densification, and possible grain uniformity of *M*-type Sr ferrite without allowing for too much grain growth and making the magnetic powder more easily aligned by the applied field. The extreme utilization of these three additives added after calcination presents the opportunity to achieve high magnetic properties (i.e., $B_r = 4608 \text{ Gauss}$, $bH_c = 3650 \text{ Oe}$, $iH_c = 3765 \text{ Oe}$, and $(BH)_{\max} = 5.23 \text{ MGOe}$) under the little Co_3O_4 addition of 1.7 wt%, which are desirable for higher-grade brushless DC motor applications, especially in modern electric vehicles.

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